

RESEARCH OF BIOCHEMICAL GOLD RECOVERY METHOD USING HIGH-ARSENIC RAW MATERIALS

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This article contains the results of experiments to recover gold from complex mineral raw materials containing more than 15 % arsenic. Laboratory tests showed that standard cyanidation recovers only 26,4 % of gold into the solution. Additional oxidizing reagents used increase the leaching efficiency and enable to recover more than 40 % of gold during subsequent cyanidation. The efficiency has been established for replacement of cyanide with thiourea and thiosulfate solutions. 79,5 %, i.e. the maximum recovery rate, was found in the experiment with preliminary oxidation with *T. Ferrooxidans*, a bacterial culture, followed by leaching with a thiourea solution.

Keywords: hydrometallurgy, biochemical method, arsenic, gold, recovery

INTRODUCTION

At present, bacterial leaching is widely used in some countries with the purpose to produce other metals commercially from ores. Intensive biohydrometallurgy studies enable to involve huge reserves of non-commercial and waste ores, as well as middlings and wastes from processing plants into processing. This method is cost-effective, reduces environmental pollution and provides an integrated use of mineral raw materials.

Iron-oxidizing bacteria as the most commonly used class of *Ferrooxidans* has numerous strains that differ in both genetics and metabolic features. Therefore, the same bacterial strain cannot serve as a universal oxidizer for absolutely all types of raw material.

That is why, it is required to breed and test iron-oxidizing bacteria strains adapted to rock mineralogy conditions, the composition of the hydrosphere and lithosphere of a particular deposit to the maximum in the biochemical technology study process.

The first commercialization of bacterial cultures in the field of gold hydrometallurgy dates back to 1986, when the BIOX® biooxidation technology was successfully applied at the Fairview gold mine in South Africa [1].

The main advantages of bacterial oxidation are the high efficiency of the ferrous iron conversion into ferric

iron, and the low cost of this technology. The prospects and efficiency of bacterial leaching are considered in the works of domestic and foreign scientists. [2-6].

Biochemical gold leaching usually combines a number of different hydrometallurgical methods where the ore is pre-concentrated, then the resulting concentrate is cleaned with acid. The pulp is washed in the presence of iron (II) sulfate, then treated with a bacterial solution containing iron (II) and a culture of *Thiobacillus ferrooxidans* bacteria, where iron (II) is oxidized by bacteria. The oxidized pulp is cyanided after water washing [7].

The study works [8] describe the pyrite and arsenopyrite oxidation mechanism at high pressure in detail. It would require to implement autoclave leaching that has a number of disadvantages (limited amount, high operating costs, and the need to increase the control over the equipment) to use it commercially. Some works [9-10] provide a review of the arsenopyrite transformations during the oxidative attack of *Acidithiobacillus Ferrooxidans* bacteria culture. The main extraction mechanism for gold-bearing sulfide minerals of pyrite and arsenopyrite in all cases occurs due to the iron oxidation.

The search for alternative cyanide-free leaching methods is one more important study area in modern gold hydrometallurgy. Leaching is performed in an acidic medium at pH = 2 - 4; thiourea is not oxidized under these conditions, and sulfuric acid solution of ferric salt $Fe_2(SO_4)_3$ is used as an oxidizing agent. The process speed directly depends on the solution pH and the concentrations of thiourea and iron (III) sulfate. The thiourea $[CS(NH_2)_2]$ complexation capacity is determined with $NH_2 - C = S$ group present in the compound. The stability of the gold thiocarbamide complex $(Au[CS(NH_2)_2]^+)$ determined by the polarographic method, is $4,4 \times 10^{22}$.

The cationic complex of gold, $Au[CS(NH_2)_2]^+$, formed with thiourea molecules has an instability con-

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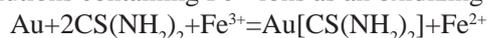
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stant equal to $3,2 \times 10^{-26}$. Therefore, the standard potential of gold in a thiourea solution decreases to +0,38 V. It explains the gold solubility in acidic aqueous thiourea solutions containing Fe^{3+} ions as an oxidizing agent:



STUDIES AND ANALYSIS

The study objects are samples of mineral raw materials taken from two sampling points in a gold ore deposit. First of all, X-ray fluorescence and chemical analyzes were performed to determine the chemical composition of the samples. The results are presented in Tables 1 and 2.

The results of Table 1 demonstrate a very high content of arsenic, sulfur and iron in both samples that is typical for high content of pyrite and arsenopyrite minerals. The chemical analysis results from Table 2 showed that the gold content in sample 1 is 4,75 g/t and in sample 2 is 5,84 g/t.

X-ray phase analysis showed some differences in the composition of the samples. The analysis revealed a clear predominance of arsenopyrite (29,2 %) quartz (16,5 %) and pyrite (10,3 %) in the first sample, the rest of the mass was accounted for various aluminosilicate inclusions. The second sample turned out to be more diverse in terms of aluminosilicate and magnetite mineral phases. The content of arsenopyrite and pyrite was 11,2 % and 6,7 %, respectively.

Table 1 Results of X-ray fluorescence analysis of samples

sample 1			
Element	/%	Element	/%
O	31,675	Fe	15,109
Na	0,821	Co	0,04
Al	4,477	Cu	0,115
Si	15,677	Zn	0,006
P	0,034	As	17,15
S	11,877	Rb	0,006
Cl	0,048	Sr	0,007
K	1,00	Zr	0,012
Ca	1,71	Sb	0,027
Ti	0,103	Bi	0,065
sample 2			
Element	/%	Element	/%
O	44,097	Cr	0,018
Na	0,862	Mn	0,018
Al	3,669	Fe	14,602
Si	12,5	Co	0,041
P	0,028	Ni	0,015
S	5,025	Cu	0,113
Cl	0,072	As	15,627
K	0,935	Rb	0,007
Ca	1,26	Zr	0,016
Ti	0,108	Bi	0,075

Table 2 Results of chemical analysis of the samples

Sample	Au / g/t	Ag / g/t	Fe / %	S / %	Cu / %
sample 1	4,75	0,92	20,9	12,72	0,1
sample 2	5,84	1,67	18,23	5,37	0,11

Scanning electron microscopy has recorded spectra of sulfur, arsenic and iron next to the gold spectra points detected for the test samples that is typical for the associations of gold with arsenopyrite (Figure 1).

Rational phase analysis was also performed to determine the form of gold in the samples. In the first sample, 82,11 % of gold is mainly bonded to mineral lattice, fine gold and visible gold in nuggets are 7,37 % each, while gold in quartz is only 3,15 %. The bulk of the precious metal is bonded to mineral lattice (76 %), gold inclusions in quartz accounts for 12 %, fine gold in nuggets accounts for 7,7 %, free nugget form is 4,3 % in the rationally phase composition of the second sample as in the first one.

Research of cyanide-free leaching using oxidizing reagents. Bacterial oxidation. Experiments using direct cyanidation with 0,1 % sodium cyanide solution served as a reference to compare with other methods. A 70 % technical mixture of trichloroisocyanuric acid (TCCA) was used as a chlorine-containing oxidant. The application of sulfanol, a surfactant, was considered among the variants for organic oxidants.

Various combinations of thiosulfate and thiourea solutions with the addition of oxidizing components served as alternative leaching reagents in the variants of cyanide-free gold recovery. Two applications of sodium chloride in combination with a thiosulfate solution were tested as additional chloride applications, and one application of ammonia solution was also tested in one of the applications. The efficiency of hydrogen peroxide as an oxidizing reagent in leaching with thiourea was studied besides the use of chlorine-containing and organic oxidants in the cyanide-free leaching process.

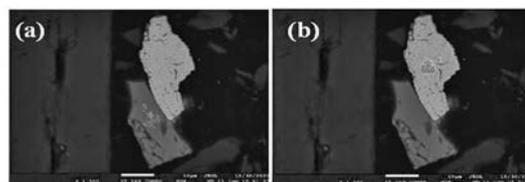


Figure 1 Scanning electron microscopic (SEM) images (a) spectra: As – 73,07 %, Fe – 15,86 %, S – 11,07 %; (b) spectra: Au- 96,41 %, Ag- 3,59 %.

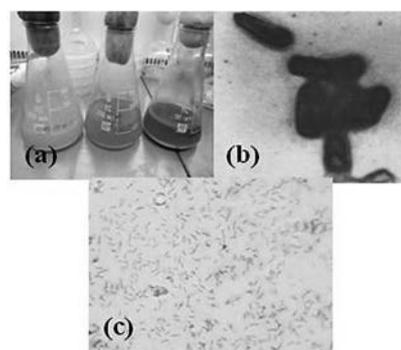


Figure 2 Selection and accumulation of bacterial biomass (a) Selection of a nutrient medium for the growth of an adapted culture of *Th. Ferrooxidans* for the test raw material; (b) General view of bacterial cells; (c) adaptation of *Th. Ferrooxidans* pure culture to arsenic under a microscope.

Table 3 Leaching conditions for gold samples with Au content of 5,84 g/t

Var. No.	Leaching parameters
1	NaCN 0,1 %
2	2 mL of H ₂ O ₂ + 1 g of CS(NH ₂) ₂
4	2 mL of H ₂ O ₂ + 0,5 g of CS(NH ₂) ₂
5	2 mL of H ₂ O ₂ + 1g/L of NaCN
6	16 g/L of NaCl + 6,7 g/L of Na ₂ S ₂ O ₃ + 7 g/L of NH ₄ OH
7	16 g/L of NaCl + 6,7 g/L of Na ₂ S ₂ O ₃
8	1,5 g of TCCA for 2 hours; 1 g/L of NaCN
9	1,5 g of TCCA for 2 hours; 0,5 g of CS(NH ₂) ₂
10	1,5 g of TCCA for 2 hours; 6,7 g/L of Na ₂ S ₂ O ₃
11	6,7 g/L of Na ₂ S ₂ O ₃ + sulfanol
12	1 g of CS(NH ₂) ₂ + 2 mL of HCl + sulfanol
13	1 g of CS(NH ₂) ₂ + 4 mL of HCl + 0,5 g of TCCA
14	1 g of CS(NH ₂) ₂ + 5 mL of HCl
15	Bacteria; 1 g of NaCN 0,1%
16	Bacteria; 1 g of CS(NH ₂) ₂
17	Bacteria; 6,7 g/L of Na ₂ S ₂ O ₃

Previous experiments for the preliminary oxidation of a sample of mature tails with a bacterial culture showed a low adaptation of the common *Ferroxidans* strain to the high content of arsenic in the composition of mineral raw materials. Due to it, a representative sample was sent to the research laboratory of Rosgeologia JSC, Moscow, for the isolation and growth of a viable strain of microorganisms, followed by bacterial acidification of the mineral raw material pulp (Figure 2).

After the selection of the adapted strain, bacterial acidification of the sorption tailings sample was performed for 10 days at a ratio of S:L = 1:2 and pH = 1,5 - 2,0. After pulp oxidation, chemical analysis of the spent bacterial solution showed the presence of the following elements: iron – 0,84 g/L, copper – 25,4 mg/L, arsenic – 1,0 g/L. The arsenopyrite minerals contained in the sample as a result of the oxidation reaction pass mainly into insoluble arsenates AsO₄³⁻ and remain in the solid phase of the pulp, while not more than 1,5 - 2,0 % of the total arsenic content passes into the solution in the oxidation process. Microbiological analysis recorded a significant reduction in living cells in the spent bacterial solution (10⁶ to 10³ C/cm³). The oxidized pulp was used in gold leaching experiments after decantation and removal of the bacterial solution. Leaching was performed with three solutions for comparative experiments:

- 1) sodium cyanide solution – 1 g/L (after pH increase up to 10,5 - 11,0);
- 2) thiourea solution – 1 g/L;
- 3) sodium thiosulfate solution – 6,7 g/L.

In total, there were 17 variants of experiments including 5 cases where sodium cyanide was used as a leaching solution for the control comparison. The conditions of the experiments are showed in Table 3.

The results of the experiments (Table 4) showed the applicability of oxidizing reagents in the leaching gold

Table 4 Results of gold leaching of samples with Au content of 5,84 g/t

Var. No.	pH	Cake Au / g/t)	E Au / %
1	10,5	4,3	26,4
2	2,1	3,86	33,9
4	2,1	3,43	41,3
5	11,0	3,5	40,1
6	9,0	3,14	46,2
7	3,0	3,25	44,3
8	1,9→10,6	3,372	42,3
9	2,1	4,308	26,2
10	3,6	4,392	24,8
11	2,0	3,672	37,1
12	1,0	4,184	28,4
13	1,0	2,92	50,0
14	1,0	3,8	34,9
15	2,0→11,0	1,78	69,5
16	2,0	1,198	79,5
17	2,0	3,05	47,8

process from refractory raw materials represented by sorption tailings. Conventional direct cyanidation considered as a reference variant yields 26,4 % recovery. Besides, variants with additional oxidation of the sample with hydrogen peroxide, TCCA, bacteria were considered to compare the methods involving the use of cyanide as the main reagent in the gold leaching process. For example, cyanidation after using hydrogen peroxide enables to extract 40,1 % of gold and 42,3 % of TCCA, and the maximum recovery (69,5 %) was observed during preliminary bacterial oxidation.

The use of a mixture of TCCA and hydrochloric acid in thiourea leaching enables to extract 50 % of gold. The maximum recovery rate, 79,5, was observed in the experiment with preliminary oxidation with *T. Ferroxidans*, a bacterial culture adapted to high arsenic content, followed by leaching with a thiourea solution.

CONCLUSION

The processing of gold-bearing raw materials with complex composition always requires additional technological operations to destroy the crystal lattices of sulfide gold-bearing minerals. Preliminary bacterial oxidation methods are widely used besides the use of chemical oxidants. However, the biological oxidation method application requires a long and complex work to adapt the bacterial culture to large amounts of arsenic in the mineral composition of the samples under study. Breeding and growing the adapted culture of *Th.Ferroxidans* allows further efficient oxidation of mineral raw materials and gold leaching with both cyanide and alternative solutions. Besides, the costs of neutralizing the final effluents and leach tailings are reduced due to the replacement of cyanide with a thiourea solution.

Biochemical leaching experiments assuming bacterial pre-oxidation showed maximum results: 69,5 % with further cyanidation and 79,5 % with thiourea leaching.

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Note: The responsible translator for English language is Nastya Kurash, Translation agency «ART Translations».